Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 56 (2014) 431 – 438

Energy Procedia

11th Eco-Energy and Materials Science and Engineering (11th EMSES)

Binary-additives Toughened Biopolymer for Packaging Application

Supakij Suttiruengwong[a,*], Sutida Pitak[a], Manus SaeDan[b], Watit Wongpornchai[a], Danattha Singho[a]

[a]*Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, 73000, Thailand*

[b]*Department of Physics ,Faculty of Science , Silpakorn University,Nakhon Pathom 73000, Thailand*

Abstract

The toughening of poly(lactic acid) or PLA with Monmorillonite clay (MMT), polyamide-block-ether (PEBAX) and hyperbranched polymer (Boltorn®) was investigated. PLA was first blended with 1, 2, 2.5, 3 and 4%wt of MMT, 5-20%wt of PEBAX and Boltorn® for a single additive system. For the binary additive system, PEBAX and Boltorn® 5-20%wt were pre-mixed with 2.5%wt of MMT, and then they were added to PLA. PLA blendes were prepared by an internal mixer. Tensile properties, impact properties and morphology of PLA blends were investigated. For single additive with PLA, adding MMT showed the increasing of toughness of PLA. PLA/PEBAX blends were shown the increasing of elongation and impact strength with containing PEBAX content, but modulus and tensile strength decreased. The results of PLA/Boltorn® blends were similar with PLA/PEBAX blends. Furthermore, elongation and impact strength of PLA blends can be improved by adding PEBAX binary additive, modulus and tensile strength decreased but not as severe as single additive. Adding Boltorn® as in a binary additive led to the brittleness and less elongation of blends when compared to adding a single additive and neat PLA.

Peer-review under responsibility of COE of Sustainalble Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)

Keywords: Bioplastic; Poly(lactic acid); toughen; Binary additive

1. Introduction

Bioplastics are generally referred to polymers that can be either biobased or biodegradable or both. For biobased property, the monomer can be derived from natural and renewable sources such as corn sugar and beets etc.[1-3], and even carbon dioxide. They also represent properties with high strength and processability similar to

* Corresponding author. Tel.: +6-634-219-363; fax: +6-634-219-363.
E-mail address: supakij@su.ac.th

1876-6102
Peer-review under responsibility of COE of Sustainalble Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)
doi:10.1016/j.egypro.2014.07.176

conventional, non-degradable fossil-based plastics. However, some properties such as brittleness, high moisture uptake and poor thermal resistance are the drawback of bioplastics derived usually from polyester types. Among those biopolymers, Polylactic acid (PLA) is the most popular and wildly available in a large scale production and products.

Poly(lacic acid) or PLA is a biocompatible, bioresorbable, and biodegradable polymer. It is polyester derived from 100% renewable source and degrades to nontoxic compounds in landfill. Moreover it represent good mechanical properties with high strength and good processability [1,3-6]. However, PLA is brittle. Thus, PLA can be modified for improve the toughness for various applications [1,3,6-8]. Many approaches was developed for toughening PLA such as co-polymer, adding additive and blending with flexible polymer. In the first approache, copolymer with same type aliphatic polymer can be prepared. The example of copolymer is PLA and polycaprolactone [6]. But making co-polymer are uneconomical method. Second approach is the polymer blends, where PLA can be blended with flexible polymer (natural rubber, elastomer), polyamide elastomer [8]. Another popular approach is adding additive such as nanoclay (rectorite, MMT). In the early study, the addition only 1-3%wt of clay increased toughness of PLA [5,9] . But up to now there have no reports that study the result of binary additives to improve toughness property of PLA.

Therefore, in this work, it was aimed to study the additives in a single and binary system to improve toughness property of PLA. Hyperbranched polyester and polyether block amide were used as blend pair and nanoclay MMT was selected as a composite.

2. Experimental

2.1. Materials

Polylactic acid (PLA2002D) was obtained from Natureworks® Co., LTD, USA. Montmorillonite (MMT), organically modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium (MT2EtOH) [9], was obtained from Connell Brothers Co., LTD , Thailand. Polyether block amide (PEBAX 3533)[8, 11] was obtained from Arkema Co., LTD, Thailand and Hyperbranch polymer (Boltorn® H30) was obtained from Perstrop Speciality Chemical AB, Sweden.

2.2. Preparation of samples

PLA, MMT, PEBAX and Boltorn® were dried at 70°C for 24 hr in a vacuum oven to remove moisture. The sample were blended in an internal mixer(Chareon Tut, Thailand) 75 rpm 7 min 170°C for PLA and 180°C for PHBV. All components in a single additive were neat PLA , PLA/MMT (1,2,2.5,3 and 4 %wt of MMT) PLA/PEBAX or Boltorn® (0-20%wt of PEBAX or Boltorn®) and for a binary additive syste, were PLA/MMT/PEBAX or Boltorn® (2.5%wt of MMT[9] and 0-20%wt of PEBAX or Boltorn®).The samples were compressed into standard micro tensile and Izod impact specimens by using a compression molding (Chareon Tut, Thailand) Model with a temperature of 170°C.

2.3. Mechanical analysis

Tensile test was carried out according to ASTM D638 using an Universal Testing Machine (model 5968, Instron Co.,LTD ,Thailand) under ambient conditions with crosshead speeds of 5 mm/min. Izod impact tests were carried out on notched impact specimens according to ASTM D256, by using Pendulum Impact Tester (Gotech Co.,LTD Model B5102.202 ,Thailand) under ambient conditions. Ten specimens of each formulation were tested and the average values reported.

2.4. Morphology analysis

For scanning electron microscope (SEM) observation, all the fractured specimens were coated with a layer of gold and observed by a scanning electron microscope (Model JSM-5410LV, JEOL, Japan). Dog bone specimens after tensile testing were used for investigating the fracture behavior. Impact specimen that immersed in liquid nitrogen and fractured was observed for cryo-fractured surface of blends.

3. Results and Discussion

3.1. Mechanical analysis

3.1.1. Tensile test

The tensile and toughness properties of were presented in Table 1. Improved properties were caused by MMT reinforcement. The elongation at break of PLA was decreased when MMT more than 2.5%wt because MMT provided more stiffness to PLA. The results were similar to a privious report elsewhere [9]. Tensile properties of PLA/PEBAX represented the dramatic decreasing of modulus, slightly decreasing of tensile strength and great increase of elongation at break and toughness. Toughness is the ability of a material to absorb energy and plastically deform without fracture, it can calculate from the area under the stress strain curve from a tensile test. PLA toughening resulted from blending with PEBAX. The ether moiety of PEBAX is a flexible part that can absorb force instead PLA matrix. Consequently, PLA toughness was improved. Adding 15%wt PEBAX resulted in the most toughened PLA. The results were in agreement with the previous reported work [8]. Except the elongation at break, it decreased when 20%wt of PEBAX was added. PLA/Boltorn® blends showed the decrease of tensile properties, even less than neat PLA with increasing Boltorn® content as shown in Table 1. The results implied that Boltorn® was unable to toughen PLA. PLA blended with 10%wt Boltorn® revealed the highest elongation at break, thus the most toughened specimen.For a binary additive system with constant MMT content at 2.5%wt, PLA blended with PEBAX binary additive showed the decrease of modulus and tensile strength and the increase of elongation and toughness with PEBAX content. PLA/PEBAX in a binary additive at 15%wt of PEBAX represented the highest toughness as show in Table 1. For Boltorn® in a binary additive, tensile properties decreased with increasing Boltorn® content.

3.1.2. Impact test

Fig. 1 shows the results of notched impact tests of PLA composites. For a single additive with PLA, adding MMT 1-2%wt showed increasing impact strength of PLA but the decrease in such properties occurred when MMT was over 2%wt. The impact strength of PLA/PEBAX blends increased when PEBAX content increased in a single additive and a binary additive system (Fig. 2). These results represented impact improvement upon adding PEBAX. However, impact strength of a single additive was higher than the binary additive system because MMT in the blend increased the stiffness to PLA matrix. For PLA/Boltorn®, adding Boltorn did not improve impact properties of PLA , for all cases. The impact testing demonstrated that the binary additive of PEBAX and MMT can still improve impact properties to PLA

Table 1. Tensile and toughness properties of PLA in a single and binary additive system.

Specimens	Young's Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Toughness (MJ/m^3)
Neat PLA	807.75 ± 6.65	64.20 ± 1.71	15.65 ± 0.82	6.659 ± 0.00
PLA1M	835.63 ± 5.40	68.12 ± 1.53	19.61 ± 1.66	9.272 ± 0.01
PLA2M	865.27 ± 11.7	73.61 ± 1.94	20.62 ± 5.34	11.79 ± 0.01
PLA2.5M	875.33 ± 8.73	77.96 ± 1.49	22.65 ± 2.07	12.91 ± 0.00
PLA3M	899.21 ± 13.0	81.70 ± 1.54	15.58 ± 0.78	8.173 ± 0.00
PLA4M	898.52 ± 25.2	86.23 ± 2.21	15.86 ± 0.89	9.294 ± 0.00
PLA5P	339.98 ± 9.30	55.74 ± 0.93	77.28 ± 24.1	35.44 ± 0.03
PLA10P	340.10 ± 9.41	48.16 ± 1.16	133.5 ± 28.7	44.76 ± 0.02
PLA15P	325.05 ± 18.3	41.20 ± 1.77	173.0 ± 19.9	59.88 ± 0.03
PLA20P	301.17 ± 6.44	37.21 ± 0.81	157.2 ± 17.4	56.05 ± 0.06
PLA5B	673.40 ± 10.8	53.60 ± 1.73	18.96 ± 0.21	5.458 ± 0.00
PLA10B	324.69 ± 13.5	57.11 ± 1.55	21.79 ± 1.07	6.793 ± 0.01
PLA15B	336.59 ± 22.8	38.67 ± 1.65	13.63 ± 0.68	2.685 ± 0.01
PLA20B	321.32 ± 13.6	25.89 ± 3.41	9.950 ± 0.61	1.413 ± 0.00
PLA2.5M5P	734.80 ± 20.5	46.22 ± 1.33	16.40 ± 1.62	4.481 ± 0.00
PLA2.5M10P	667.60 ± 8.79	41.44 ± 0.55	30.38 ± 3.50	9.307 ± 0.00
PLA2.5M15P	608.40 ± 10.2	34.22 ± 0.73	31.30 ± 3.25	9.076 ± 0.00
PLA2.5M20P	529.00 ± 17.6	27.82 ± 0.98	42.24 ± 1.74	9.100 ± 0.00
PLA2.5M5B	745.40 ± 14.9	49.66 ± 0.59	8.290 ± 0.39	2.203 ± 0.00
PLA2.5M10B	707.20 ± 6.69	45.10 ± 0.31	15.48 ± 1.04	5.025 ± 0.01
PLA2.5M15B	646.00 ± 14.5	38.66 ± 1.52	7.22 ± 0.62	1.595 ± 0.00
PLA2.5M20B	617.80 ± 5.63	35.96 ± 0.86	8.62 ± 0.86	1.840 ± 0.00

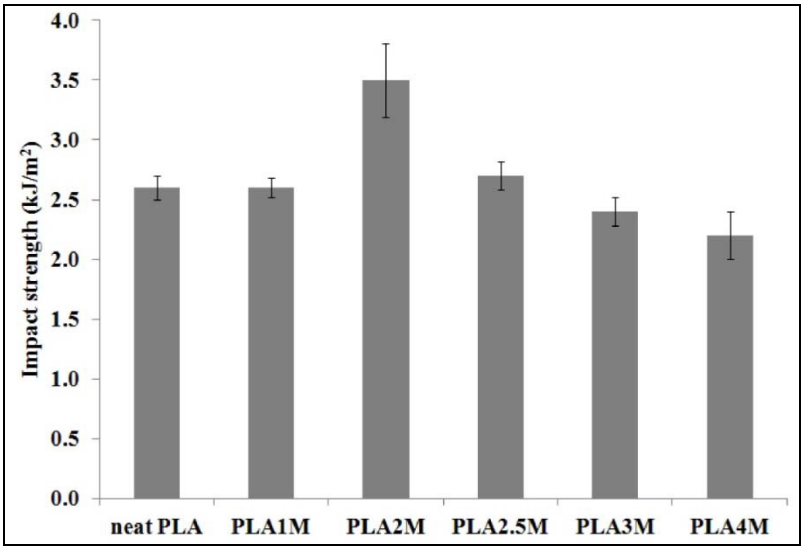

Fig. 1. Impact strength of PLA-clay composite

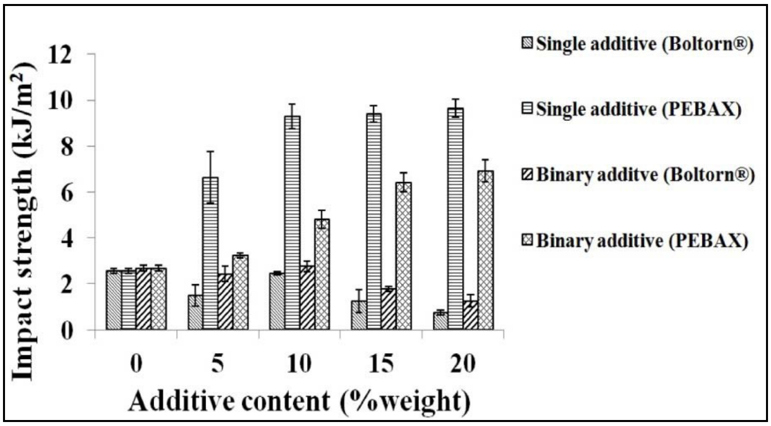

Fig. 2. Impact strength of PLA blends.

3.2. Morphology analysis

Cryo-fracture of neat PLA and PLA/single additive blends are shown in Fig.3, there were MMT some agglomerated in PLA as shown in Fig.3b. PLA/PEBAX(Fig.3c) blends showed good distribution of spherical PEBAX particles in PLA matrix and had good adhesion with PLA [8], thus PLA/PEBAX blends showed toughness improvement in tensile testing and impact strength in impact testing because PEBAX rubber phase can absorb impact force and delayed the fracture of PLA matrix. For PLA/Boltron blends, cryo-fracture in Fig.3d showed well distribution of Boltorn® phase but some Boltorn® were agglomerated to be big spherical particle and almost particle are wiped from surface that mean bad adhesion between Boltorn® particles and PLA matrix. The agglomerate and bad adhesion of Boltorn® is reason for bad tensile properties of PLA/Boltorn® blends but Boltorn® particles were harder than PEBAX, thus the decrease of the modulus were not as severe as in case of PLA/PEBAX. Although Boltorn® are not rubber but their structure have free volume more than PLA, so PLA/Boltorn® showed some impact improvement when compare with neat PLA. Cryo-fracture of PLA/binary additive are shown in Fig.4. PLA matrix still show good adhesion for MMT and PEBAX and PEBAX are better distribution than single additive system that PEBAX appeared very tiny spherical particles, as shown in Fig.4a , so PLA/PEBAX showed improvement of toughness and blends can maintain high modulus and tensile strength because stiffness of MMT. PLA/PEBAX binary additive blends showed impact strength improvement. Although the impact strength was lower than adding only PEBAX alone. PLA/Boltorn® binary additive's cryo-fracture was showed in Fig.4b, Boltorn® particles had well dispersion that see from distribution of spherical particles, but distribution of Boltorn® particles less than PEBAX particles

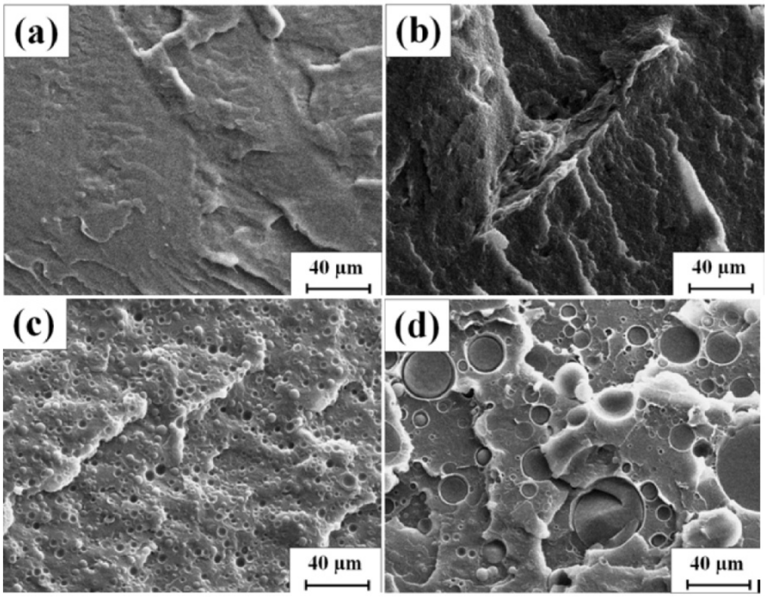

Fig.3 Cryo-fracture of PLA/single additive blends ; (a) Neat PLA; (b) PLA2.5M; (c) PLA15P and (d) PLA15P

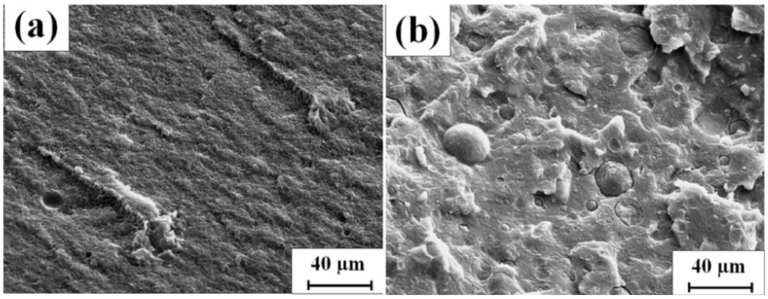

Fig.4 Cryo-fracture of PLA/binary additive blends ;
(a) PLA2.5M20P; (b)PLA2.5M20B

3.3. Morphology analysis

Tensile fracture of neat PLA and PLA/single additive blends are shown in Fig.5. PLA/MMT blends (Fig.5b) showed pull out of few fibril from fracture surface, compared with neat PLA in Fig.5a . It showed that MMT can change fracture behaviour of PLA from brittle fracture to more ductile fracture. Adding PEBAX in PLA showed ductile fracture, PLA/PEBAX blends image (Fig.5c) represented fibrils were drawn out from fractured surface, indicating the improvement of toughness by PEBAX. That made PLA more elongated and energy at break than neat PLA [8]. PLA/Boltorn® image showed the brittle fracture in Fig.5d . Fracture surface of PLA/Boltorn® showed smooth surface and Boltorn® phase was separated from PLA matrix because the poor adhesion force of PLA/Boltorn® compared to that of PLA/PEBAX. Fig.6 showed tensile fracture surface of PLA/binary additive blends. PLA/PEBAX binary additive in Fig.6a represented the fibril similar to PLA/PEBAX single additive but the fibrils were shorter than that of single additive system. This indicated the toughening was occurred by adding PEBAX in a binary additive. However, Boltorn® binary additive showed the same result obtained in the single additive system. PLA/Boltorn® binary additive blends fracture surface (Fig.6b) was smooth and did not have any fibril. PLA can bear lower strength and easy to be fractured. The results inndicated that PLA could be toughened by adding PEBAX for the binary additive, whereas Boltorn® did not operate the same task

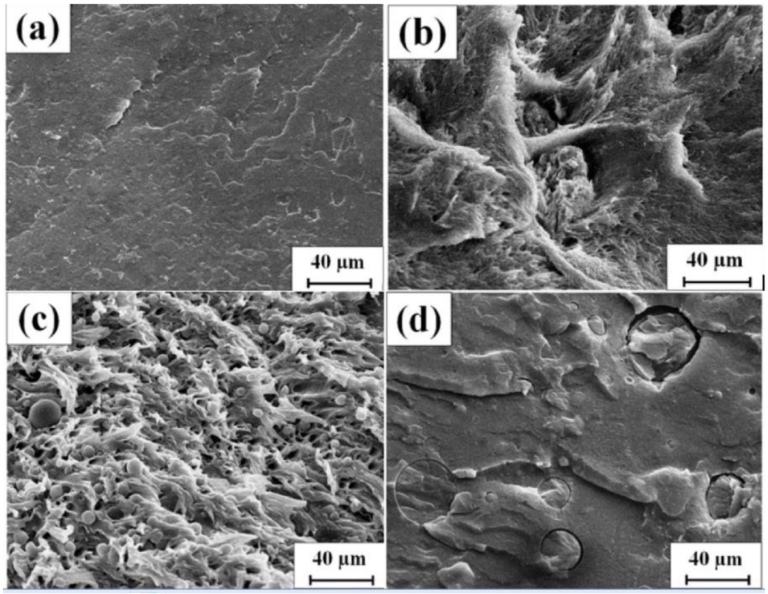

Fig.5. Tensile fracture of PLA/single additive blends ;
(a)Neat PLA; (b) PLA2.5M; (c) PLA15P and (d) PLA15B

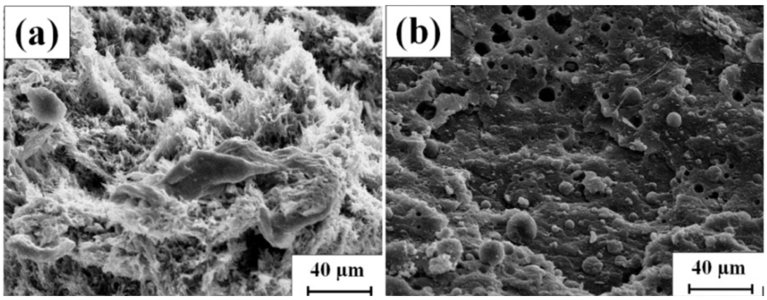

Fig. 6. Tensile fracture of PLA/binary additive blends;(a) PLA2.5M20P; (b) PLA2.5M20B

4. Conclusions

PLA added PEBAX in the binary additive showed the improvement of toughness as indicated by the increase of elongation, toughness and impact strength when increase PEBAX content in blends, and the blends could still maintain high tensile strength and modulus. The binary additive of PEBAX and Montmorillonite can toughen PLA matrix.

Acknowledgements

The authors would like to thank the department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University for financial support and instrument and laboratory to conduct this research.

References

[1] Arends, C.B., *Polymer toughening*. Plastics engineering. 1996, New York: Maecel Dekker, Inc.
[2] Meng, B., et al., *Transparent and ductile poly(lactic acid)/poly(butyl acrylate) (PBA) blends: Structure and properties.* European Polymer Journal, 2011. 48: p. 127–135.
[3] Rasal, R.M., A.V. Janorkar, and D.E. Hirt, *Poly(lactic acid) modifications.* Progress in Polymer Science, 2010. 35(3): p. 338-356.
[4] Balakrishnan, H., et al., *Novel toughened polylactic acid nanocomposite: Mechanical, thermal and morphological properties.* Materials & Design, 2010. 31(7): p. 3289-3298.
[5] Li, B., et al., *Organically modified rectorite toughened poly(lactic acid): Nanostructures, crystallization and mechanical properties.* European Polymer Journal, 2009. 45(11): p. 2996-3003.
[6] Meng, B., et al., *Toughening of polylactide with higher loading of nano-titania particles* ***coated by*** *poly([epsilon]-caprolactone).* Materials Letters, 2010. 65(4): p. 729-732.
[7] Oyama, H.T., *Super-tough poly(lactic acid) materials: Reactive blending with ethylene copolymer.* Polymer, 2009. 50(3): p. 747-751.
[8] Zhang, W., L. Chen, and Y. Zhang, *Surprising shape-memory effect of polylactide resulted from toughening by polyamide elastomer.* Polymer, 2009. 50(5): p. 1311-1315.
[9] Jiang, L., J. Zhang, and M.P. Wolcott, *Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms.* Polymer, 2007. 48(26): p. 7632-7644.
[10] Murariu, M., et al., *Polylactide (PLA)-CaSO4 composites toughened with low molecular weight and polymeric ester-like plasticizers and related performances.* European Polymer Journal, 2008. 44(11): p. 3842-3852.
[11] Arkema. *PEBAX Polyether block amides*. Product properties 2006 [cited 2006; Available from: http://www.PEBAX.com.